

WHICH OXYGENATE IS RIGHT FOR YOU?

Elaine J. Chang
Petrochemicals, Polymers, and Energy Center
SRI International
Menlo Park, California 94025

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INTRODUCTION

Recent announcements of additional sources of oxygenates have generated considerable interest. Increasing demand for methyl tert-butyl ether (MTBE) worldwide, especially in the United States for oxygenated fuel and reformulated gasoline (RFG), provides the primary incentive for technologies that produce additional raw material (namely isobutene) and/or alternative oxygenate compounds. Normal butene isomerization and diisopropyl ether (DIPE) are two new processes introduced in 1992 to meet the oxygenate demand.

The U.S. Clean Air Act Amendments of 1990 (CAAA) have created a huge demand for capital. Between 1991 and 2000, the U.S. refining industry will need to make capital expenditures of about \$37 billion (1990 dollars) to meet refinery regulatory requirements, and to manufacture reformulated gasoline and ultra-low sulfur diesel fuel.⁽¹⁾ To obtain financing, whether internally or from external sources, projects must provide sound economics and pose minimal technological risks. These concerns have prevented several large MTBE projects, involving both established and new technologies, from going forward.⁽²⁾

The introduction of normal butene isomerization and DIPE processes has generated a great deal of enthusiasm, but neither process had been licensed by the third quarter of 1993. Technology risk is a major barrier to obtaining financing inasmuch as lenders are unlikely to finance the first commercial application of any technology. Currently, Texas Olefins/Phillips Petroleum and Lyondell have demonstrated normal butene isomerization on a commercial scale in their plants. However, Mobil has not demonstrated the DIPE process beyond the pilot plant stage.

In this paper, we assess the technological aspects of normal butene isomerization and DIPE processes, and compare their economics with existing etherification processes.

DRIVING FORCES FOR USE OF OXYGENATES IN GASOLINE

Additives and improved refining processes have long been used to improve gasoline quality. Figure 1 shows how gasoline octane has been improved historically. To achieve widespread use, a new additive or process improvement must prove its economic worth. The addition of lead to increase gasoline octane was one of the most cost-effective methods, and its use was nearly universal until the detrimental environmental effects of lead became apparent.

The reasons for using oxygenates in gasoline have varied over time. Alcohols were added to commercial gasoline on an experimental basis as early as 1924. In response to the shortage of crude oil during the oil crises of 1973 and 1979, alcohols were promoted for use either as a substitute or a partial replacement for gasoline. Brazil developed the most significant program, which called for ethanol to be substituted for a large percentage of the gasoline consumed in that country. In the United States, a federally subsidized program was established to encourage the use of ethanol in gasoline nationwide. Although both the Brazilian and the U.S. ethanol programs are still active, the high cost associated with the use of ethanol constitutes a major disadvantage. Consequently, some form of monetary subsidy is required for acceptance of ethanol fuel.

During the mid-1980s, some U.S. gasoline marketers tried to introduce methanol into their gasoline. Both direct blending and cosolvent blending (methanol with tert butyl alcohol [TBA] to minimize phase separation) were tried. These blends were economically attractive because the cost of methanol was considerably lower than that of gasoline. However, compatibility and mechanical problems, together with limited availability of the cosolvent, prevented widespread acceptance of the use of methanol in gasoline.

Ethers, principally MTBE, became widely available in the early 1980s. They have gradually gained acceptance as gasoline blending agents because they offer high octane and excellent gasoline compatibility, and because they can be partially made from refinery by-product isobutene at a cost similar to the cost of producing toluene, whose octane quality is similar to MTBE in gasoline. Refiners originally began to

investigate the use of MTBE as an octane enhancer blended into gasoline at levels of 7 to 10%. Other ethers, such as ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME), are newer products with gasoline blending properties somewhat similar to those of MTBE.

In the 1980s, the improved burning characteristics (more complete combustion) of MTBE-gasoline blends and their potential for reducing carbon monoxide and smog formation became recognized. Consequently, oxygenated fuel was adopted in the 1990 CAAA.

The CAAA requires the use of oxygenates in gasoline for environmental reasons. Most other countries will probably use oxygenates only for octane enhancement until the full environmental consequences of oxygenated and reformulated fuels are better understood.

EXISTING ROUTES FOR PRODUCING OXYGENATES

MTBE, produced by reacting isobutene with methanol, is the most widely used oxygenate. Isobutene, which is the critical raw material in meeting the demand for MTBE, is available from three commercial sources. By-product sources include mixed C₄ streams available from (1) catalytic cracking in refinery gasoline production, (2) steam cracking for ethylene production, and (3) TBA and propylene oxide (PO) production (dehydration of TBA, a coproduct with propylene oxide via the hydroperoxidation of isobutene). The rapid depletion of these traditional isobutene sources has led to the development of on-purpose isobutene production from field or mixed butanes. The dehydrogenation route to MTBE is a rapidly growing source of isobutene.

Figure 2 shows the world distribution of MTBE production by isobutene source. In the United States, dehydrogenation is now the major source for MTBE (40%), with fluidized catalytic cracker (FCC) and TBA/PO isobutene sources contributing about equal amounts (24% and 25%, respectively), and the remainder from steam cracking (11%). Dehydrogenation is also the major source of isobutene for regions rich in natural gas (e.g., Latin America, the Middle East). In contrast, ethylene cracking is a major source of isobutene in Europe and the Asia-Pacific region for MTBE productions. In these two regions, naphtha is the predominant feedstock in ethylene cracking with relatively high amounts of C₄ by-product, and FCC units are not as prevalent as in the United States.

Other ethers, such as TAME and ETBE, are based on similar technology as MTBE production. Potentially, TAME could be a large source of oxygenate in the United States. The use of ETBE faces two obstacles: (1) it competes with MTBE for isobutene, and (2) its economics depend in large part on government subsidies.

NEW ROUTES TO PRODUCE OXYGENATES

As we approach 1995, when reformulated gasoline regulations take effect in the United States, oxygenated gasoline and RFG will both become required by law, and MTBE supplies will tighten. Refiners may have no choice but to pay a premium above MTBE's octane value to obtain sufficient MTBE. As a result, many refiners are rushing to install their own oxygenate production capacity.

Isobutene is produced in refineries mainly in FCC units. In the United States, a shortage of refinery captive isobutene had kept MTBE plants' utilization rate low (i.e., 60% to 67% for 1988 through 1990).⁽³⁾ To increase FCC isobutene production, higher FCC riser temperature or isobutene-selective catalysts can be used to raise the isobutene yield by 50-200%. Two drawbacks are the additional investment needed to debottleneck the FCC unit and reduced gasoline yield.

An alternative route is the isomerization of normal butene to isobutene. In addition, other oxygenates, which do not require isobutene as raw material, such as DIPE, can be considered.

Normal Butene Isomerization

Since March 1992, six companies—Lyondell, Phillips/Texas Olefins, Mobil, IFF, UOP, and Snamprogetti—have announced the development of one-step processes to isomerize normal butenes to isobutene. The 4-carbon monoolefins have 4 isomers: 1-butene, cis-2-butene, trans-2-butene, and isobutene. Isomerization of one of the butene isomers to increase the supply of another has long been practiced commercially. For example, refineries maximize the octane number of hydrofluoric acid alkylate by installing a butene isomerization unit (e.g., the Hydrisom process) upstream of the alkylation unit. The isomerization process converts 1-butene to 2-butene, the preferred HF alkylation feedstock.

Normal butene isomerization has been extensively researched, with a variety of catalysts developed to overcome some technological difficulties—low conversion (equilibrium-limited reactions), rapid catalyst deactivation, and undesirable side reactions such as disproportionation and polymerization. The mandates for oxygenated fuels have renewed interest in this process. As MTBE production exhausts the available supplies of isobutene from traditional sources, additional isobutene is being produced on-purpose from field butanes through isomerization to isobutane and dehydrogenation to isobutene. Dehydrogenation is a very capital-intensive, and thus expensive route to MTBE. Consequently, much interest has been generated by the announcement of a new route to produce isobutene by butenes isomerization.

Normal Butene Isomerization Thermodynamics

Butenes isomerization is equilibrium limited. The equilibrium composition changes only slowly with temperature. For normal butene isomerization to isobutene, the yield in a single pass is limited to between 40 and 50 mol% in the normal reaction temperature range of 350-550°C (662-932°F). The branched isomer is favored by lower temperatures, but a faster reaction rate is favored at higher temperatures.

When the carbon skeleton is rearranged, mixtures of butenes result. Skeletal isomerization involves C-C bond rupture and reformation. Once a carbonium ion is formed in the presence of a strong acid, several side reactions also take place (e.g., polymerization, isomerization, hydrogen transfer). Therefore, it is unlikely to achieve a clean product slate. The typical isobutene selectivity ranges between 85 and 90%.

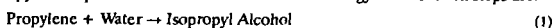
Table 1 lists processes offered for licensing, and Table 2 summarizes reported yields. These processes differ in conversion, selectivity, cycle length, and catalyst regeneration methods.

Diisopropyl Ether

In March 1992, Mobil Research & Development Corporation announced the development of a new process to produce DIPE by direct hydration of propylene to isopropyl alcohol (IPA), followed by etherification using shape-selective zeolite catalysts. DIPE's high octane and low vapor pressure gasoline blending qualities make it an attractive oxygenate blending candidate for reformulated gasoline mandated by the CAAA. Table 3 compares the blending properties of DIPE with MTBE, ETBE, and TAME. Another claimed advantage of DIPE is that, unlike MTBE, ETBE, and TAME, it is a completely refinery-based oxygenate, with no outside alcohol supply required.

UOP also unveiled a DIPE process in 1993. Its process is probably based on Union Carbide's IPA process.

Catalytic hydration of propylene to produce IPA is an established technology. The reaction steps are:



The direct propylene hydration to IPA and DIPE is thermodynamically limited with IPA as the main product and DIPE as a by-product. The use of a strong acidic catalyst can achieve direct propylene hydration under the moderate temperatures and pressures favorable to propylene conversion. Pressure is an important parameter determining propylene conversion—higher pressures increase the propylene conversion per pass. The water/propylene ratio is used to control IPA and DIPE production. A high water/propylene ratio favors IPA production, and a low ratio favors DIPE formation. The presence of excess water inhibits oligomer formation. The reaction temperature is normally kept as low as possible to minimize polymerization.

Although the hydration of propylene to IPA and DIPE is a known technology, the product recovery scheme is more complex than other etherification processes. The reactor effluent contains a mixture of unreacted feed (propylene and water), products (DIPE and IPA), and by-products (oligomers which are mainly C₆ olefins). Separating these components requires multiple distillation and extraction operations because binary azeotropes form between water/IPA, IPA/DIPE, and DIPE/water, and together they form a ternary azeotrope. Consequently, many separation schemes have been developed in order to reduce process complexity and operating cost.

OXYGENATE ECONOMICS

Figure 3 summarizes oxygenate product values for MTBE, ETBE, TAME and DIPE, including 10% depreciation and 25% pretax rate of return on investment. All economics are based on U.S. Gulf Coast overnight construction in 1993.

MTBE Economics

The product values of MTBE, based on isobutene from refinery C_4 s, steam cracker C_4 s, TBA/PO, normal butene isomerization, and field butanes, are shown in Figure 3. The economics are developed for 2,400 b/d MTBE unit based on by-product isobutene, and 12,500 b/d MTBE plant from on-purpose isobutene—typical unit sizes for these applications. The value of isobutene is based on its value in alternative process uses. The major use for isobutene in refineries is alkylation feed. This comparison provides a picture of the current competitive situation.

From this comparison, we can conclude that MTBE production based on by-product isobutene sources is the least costly route. MTBE produced from isobutene derived from TBA/PO is the least expensive at an estimated product value of 70¢/gal. MTBE derived from steam cracking and FCC by-product isobutene has slightly higher product values of 74¢/gal and 78¢/gal, respectively. MTBE product values based on either an integrated normal butene isomerization unit or a dehydrogenation unit are of similar magnitude at \$1.10/gal and \$1.09/gal, respectively. These last two processes are considerably more costly than the traditional by-product isobutene sources. Integrating MTBE production with normal butene isomerization incurs higher raw material costs because normal butenes have a high alternative value as alkylation feedstock. Dehydrogenation technology uses less costly normal butanes as raw material, but is a highly capital-intensive process.

TAME Economics

TAME, a high octane, low vapor pressure oxygenate, is becoming the second fastest growing oxygenate behind MTBE. Under the forthcoming complex model for RFG, amylene will probably be restricted in the gasoline pool because of their high Reid vapor pressure (RVP) and high atmospheric reactivity. Factors for TAME's rapid growth are:

1. It removes light olefins in gasoline, which may be limited in RFG because of the high ozone formation tendency.
2. It provides an additional source of oxygenate without competing for isobutene.
3. The alternative for light olefins removed is C_3 alkylation, which is less attractive [alkylation of C_3 s increases acid consumption, and the slight octane improvement (90 versus 87 $(R+M)/2$), does not justify the additional processing cost].

Both as an oxygenate and as an octane enhancer, TAME's economics are attractive. TAME's product value is estimated to be 75¢/gal and 81¢/gal, based on isoamylene value use as an alkylation unit feed and a gasoline blending component, respectively. The product value of TAME is competitive with that for MTBE if isoamylene is valued as the alkylation feedstock—the more likely scenario for the future.

ETBE Economics

Interest in ETBE has increased since the U.S. Treasury Department approved a 54¢/gal tax credit for ethanol used to produce ETBE. A similar tax credit is already allowed for ethanol used directly in gasoline blending. ETBE is preferred over ethanol as a blending component because it has a low vapor pressure (4 versus 19 psi). The tax credit extension makes production of ETBE more competitive with MTBE.

ETBE competitiveness hinges on the cost of ethanol. Currently, ETBE economics can be evaluated on the basis of three ethanol costs. Figure 3 illustrates that the product values of ETBE are estimated to be 83¢/gal for a 54¢/gal federal and state subsidy, \$1.03/gal for a 20¢/gal state subsidy only, and \$1.11/gal with no subsidy. ETBE is competitive with MTBE production from by-product derived isobutene only if ethanol continues to receive both federal and state subsidies. The subsidies make refinery operations dependent on government policy because the differential between methanol and grain-derived ethanol is unlikely to decrease substantially in the near future.

DIPE Economics

One of DIPE's main attractions is that it is a totally refinery-based oxygenate process. Although inexpensive water provides the source of oxygen for DIPE, propylene is a relatively high valued raw material. In addition to its value as fuel products (e.g., LPG or feed to an alkylation unit), purified polymer grade propylene is an important commodity in the basic petrochemical industry. We estimate 308,000 b/d of

propylene is produced by FCC units in the U.S. refineries. Of this quantity, 48% is used in motor fuel either as alkylate or as polymer gasoline, 45% is used as chemical feedstock, and 8% is used in liquefied petroleum gas (LPG).

Figure 3 shows that DIPE economics are sensitive to propylene feedstock cost. DIPE product value varies from 74¢/gal, \$1.09/gal, and \$1.11/gal for propylene valued as fuel, alkylate feedstock, and polymer grade product, respectively. Our valuations indicate that DIPE is not competitive with MTBE in the United States where propylene is unlikely to be valued as fuel.

CONCLUSION

Before November 1, 1992, MTBE was used mainly as an octane enhancer for gasoline. Historical MTBE prices have been consistent with its octane blending value. This relationship existed because refiners could always choose between using MTBE or changing their operations to increase the octane of their gasoline pools. MTBE's oxygen value is unclear at this time, even though the United States has already gone through one winter with mandatory oxygenated fuel. Stockpiling before the 1992-1993 winter season and low gasoline prices combined to cause the MTBE price to collapse. The average 1993 MTBE price—between 70¢/gal and 75¢/gal—is below its octane value.

Figure 4 shows the values of various gasoline blending components as a function of their octane number. The economic risks of MTBE (by-product derived isobutene) and TAME are somewhat reduced because they can always be blended into the gasoline pool at their octane value. However, a price premium for oxygen content is required to justify the building of MTBE plants based on either normal butene isomerization or dehydrogenation technologies, and DIPE. ETBE economics are precarious because the federal subsidy for ethanol will expire in 2002. The continuation of subsidies depends strongly on corn state lobbying and the U.S. budget deficit.

LITERATURE CITED

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- (2) P.R. Wilkes, "MTBE Plant financing Requires Effective Risk Management," *Fuel Reformulation*, July/August 1992, pp. 19-23.
- (3) "NPR Reports on MTBE Utilization and Capacity; 22 U.S. Plants Report," *Hydrocarbon Processing*, July 1991, p. 33.

Table 1 NORMAL BUTENES ISOMERIZATION LICENSORS		
Process Name	Developer	Licensar
Skeletal Isomerization	Lyondell	CDTech
SKIP	Phillips/Texas Olefins	Phillips
ISOFIN	BP and Mobil	Kellogg
Butesom	UOP	UOP
ISO-4	IFP	IFP
SISP-4	Snamprogetti	Snamprogetti

Table 2 NORMAL BUTENES ISOMERAZATION PROCESS CONDITIONS					
	SKIP	Skeletal Isomerization	ISOFIN	SISP-4	Equilibrium
Temperature, °C	480-550	370-440	350-430	450-490	350-520
Conversion, %	35	44	55-50	40-30	55-40
Selectivity, %	85-90	90	85-90	88-92	

Table 3 BLENDING PROPERTIES OF OXYGENATES						
	Ethers				Alcohols	
	MTBE	ETBE	TAME	DIPE	Methanol	Ethanol
Boiling point, °C	55.2	71.7	86.1	68	65	78
Density at 20° C, g/cm ³	0.74	0.75	0.77	0.73	0.79	0.79
Molecular weight	88	102	102	102	32	46
Oxygen content, wt%	18.2	15.7	15.7	15.7	50	35
Heat of combustion, cal/g	8,940	9,440	8,408	9,100	5,423	7,094
Octanes						
Blending RON	118	119	112	110	126	129
Blending MON	102	103	99	97	101	101
Blending (R + M)/2	110	111	105.5	103	115	114
Blending RVP, psi	8	3.5	1	5.0	60	18
Maximum concentration, vol%	15	13	12	—	5	5

Figure 1
IMPROVEMENT IN GASOLINE OCTANE, 1910-1990

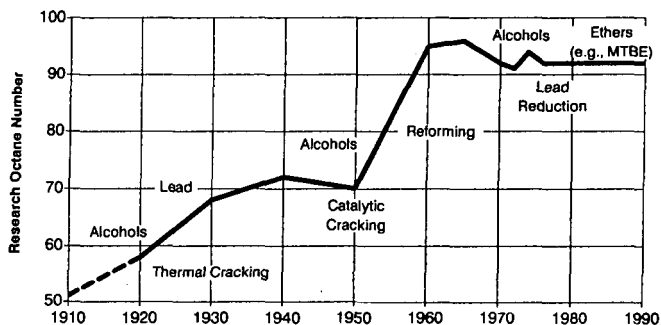


Figure 2
WORLDWIDE MTBE PRODUCTION BY ISOBUTENE SOURCE

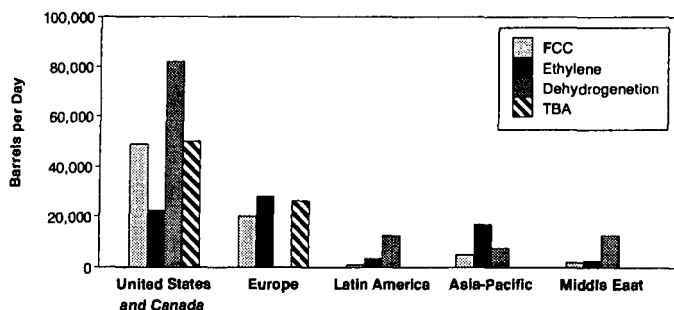


Figure 3
OXYGENATE PRODUCT VALUES: U.S. GULF COAST, 1993

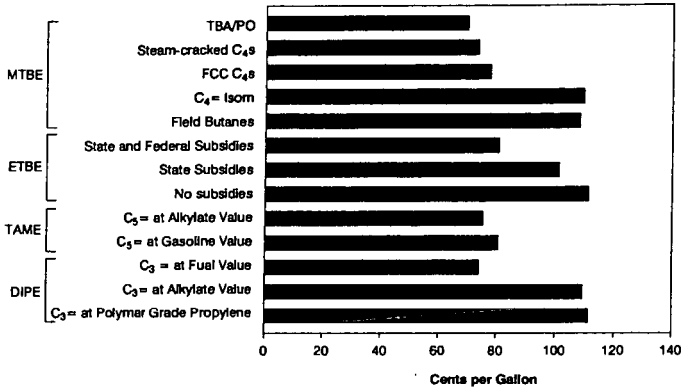
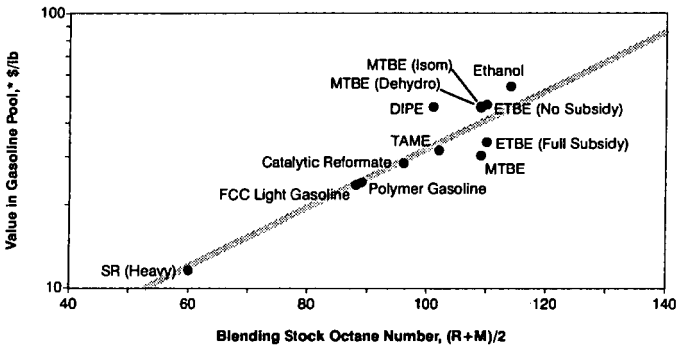


Figure 4
VALUE OF GASOLINE POOL COMPONENTS AS A FUNCTION OF OCTANE NUMBER, 1993



* Based on regular unleaded gasoline price of \$23.10/barrel.